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THE HARRIS CENTRE
Memorial University

PRODUCTION OF BIOMATERIALS FROM SOLID BIOMASS WASTES FOR THE MINING INDUSTRY

Shafiq Alam, Ph.D., P.Eng.

March 2013

This research project was funded under the The Harris Centre – MMSB Waste Management Applied Research Fund. The intellectual property vests with the author(s). For more information about this Research Fund to obtain hard copies of this report, please contact the Harris Centre.

FINAL REPORT

Production of Biomaterials from Solid Biomass Wastes for the Mining Industry

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Project Funding: **Harris Centre/MMSB Applied Research Fund (2011 – 2012)**

Report Submitted to:

Robert Greenwood
Director
The Harris Centre
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Report Submitted by:

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Date: March 31, 2012

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SECTION 1: EXECUTIVE SUMMARY

Title of Research Project:

Production of biomaterials from solid biomass wastes for the mining industry.

Background of Research:

Newfoundland and Labrador has very rich mineral resources. The mining industry in this province produces more than a dozen different mineral commodities. On the other hand, this province is producing huge amounts of solid biomass wastes everyday. Some of them are re-used, but mostly they are land-filled. With innovative, applied research these biomass wastes can be turned into more value added products for the mining industry. For example, wood wastes/saw dust, waste paper and waste cotton are some solid wastes that can easily be converted into high-tech biomaterials (bioadsorbents) for gold recovery from a dilute solution. Those solid wastes are cellulosic, they have a strong affinity to gold when converted to its functional group in a very simple and cheap process.

In this project, we have carried out some innovative applied research to produce bioadsorbents derived from solid biomass wastes, such as waste paper, waste cotton and waste wood/saw dust, which are abundantly available in this province and need proper management to increase their life-cycle. Every day tons of waste paper and cardboard are being generated. Sources of waste cotton are old cloths, waste medical bandages, etc. Wood waste is also very abundant in this province. When compared with the ever increasing gold prices (currently ~$1700/oz), the face value of these solid wastes will jump from garbage to hi-tech market value. Proper management and effective use of such solid biomass wastes as valuable bioadsorbents will not only reduce the volume of wastes being generated every day, but will also have a high end value to the gold mining industry as this cheap bioadsorbent will have superior performance over the traditionally used activated carbon. Both the mining and waste management companies in this province will benefit from this research.

Overall Project Update:

This project was supported by the Harris Centre/MMSB Applied Research Fund (2011 – 2012). The total project cost was $15,000 and the project duration was from February 01, 2011 – March 31, 2012. The following personnel were involved in this project:

Principal Investigator:	Dr. Shafiq Alam, Memorial University
Co-investigator:	Prof. Katsutoshi Inoue, Saga University, Japan
Research Assistant:	Mirza Hossain, Memorial University
Co-op Student:	Julie Kean, Memorial University
Co-op Student:	Christina Blanchard, Memorial University

In addition to research assistant and co-op students, two master's students named Omit Mehfuz and Shuaihong Yao were partly involved in this project. Christina was fully funded through this project. Mirza received partial support from another project funded by the Department of Natural Resources. Omit was self-funded student and Shuaihong was funded through the Process Engineering Design and Research Laboratory (PEDRL) grant. Julie received 50% of her salary from this PEDRL fund. In this way, the Harris Centre-MMSB fund helped attract more funding from other sources.

Research Activities:

This research work was divided into three areas for the production of biomaterials using three different types of solid waste feed materials. The prepared biomaterials (bio-adsorbents) were used to investigate their ability for gold adsorption. Those feed materials are:

1. Saw dust/waste wood
2. Waste paper
3. Waste cotton

At Memorial, Dr. Alam and his team members used waste wood/saw dust, waste paper and waste cloths (Cotton) to prepare the biomaterials (Bio-adsorbents). Prof. Katsutoshi Inoue who is the co-investigator of this project investigated paper and cotton gels in separate projects at Saga University, Japan in collaboration with Dr. Alam. All those research works progressed very well and we received excellent results based on what we submitted/published several peer-reviewed journal and conference proceeding papers as mentioned in the "Publications" section below. Details of these research activities are presented in Sections 2 and 3 later in this report.

Knowledge Mobilization:

As a part of knowledge mobilization, on June 30, 2011, two (2) students (Mirza and Shuaihong) who worked in this Harris Centre-MMSB Waste Management Fund project presented some of their research findings in a Process Mining Symposium at Memorial.

Deliverables:

1. *S. Alam*, "Production of Biomaterials from Solid Biomass Wastes for the Mining Industry", *Midterm Project Report to the Harris Centre at Memorial University* (2011).

2. *S. Alam*, "Production of Biomaterials from Solid Biomass Wastes for the Mining Industry", *Final Project Report to the Harris Centre at Memorial University* (2012).

3. *All publications* as listed in the "Publications" section below.

Publications:

1. **M. Hossain**, ***S. Alam*** and W. Kelly, "Adsorption of Gold from Aqueous Solution Using Bio-adsorbent Prepared from Red Pine Wood Dust", *Journal of Bioresource Technology* – (Manuscript prepared and is ready to submit).

2. **M. Hossain**, **S. Yao**, ***S. Alam*** and Y. Zhang, "Recovery of Gold from Aqueous Solution using Bio-adsorbent Prepared from Wood Waste", *Proceedings of the 50th Annual Conference of Metallurgists (COM2011)* held in conjunction with World Gold, Poster Presentation, October 2-5, Montreal, QC, Canada (2011).

3. B. Pangeni, H. Paudyal, M. Abe, **K. Inoue**, H. Kawakita, K. Ohto, B.B. Adhikari and ***S. Alam***, "Selective Recovery of Gold Using Some Cross Linked Polysaccharide Gels", *Green Chemistry*, The Royal Society of Chemistry Journals, – Article in Press (Accepted on April 10, 2012),

4. B. Pangeni, H. Paudyal, **K. Inoue**, H. Kawakita, K. Ohto and ***S. Alam***, "An Assessment of Gold Recovery Processes Using Cross-Linked Paper Gel", *Journal of Chemical & Engineering Data*, American Chemical Society (ACS) Publications, 57, 796−804 (2012).

5. B. Pangeni, H. Paudyal, **K. Inoue**, H. Kawakita, K. Ohto and ***S. Alam***, "Selective Recovery of Gold(III) Using Cotton Cellulose Treated with Concentrated Sulfuric Acid", *Cellulose*, DOI 10.1007/s10570-011-9628-6 (2011).

Some pages of each publications are attached in "Appendix - A". A copy of all published papers is also given to the Harris Centre in separate files.

Proposal Submitted to Expand the Solid Biomass Waste Research:

At Memorial University, Dr. Alam in collaboration with Prof. Inoue of Saga University is establishing a research program named "Biomass NL" where different kinds of bio-adsorbents will be prepared from solid biomass wastes derived from agricultural, forestry and marine resources those are abundantly available in Newfoundland and Labrador. Those bio-adsorbents will be used for the recovery of metals from the metallurgical solution and/or polluted mine-site water. In 2010, Dr. Alam received funding from the Harris Centre to produce the bioadsorbents **derived from the agricultural biomass** wastes such as fruit residues to remove heavy/toxic metals from acid mine drainage. Current project through the Harris Centre-MMSB Waste Management Fund (2011-2012) is to produce bio-adsorbents **from the cellulosic biomass wastes** such as waste paper, waste cotton, waste wood etc. for the recovery of precious metals. To expand this "Biomass NL" program, so far Dr. Alam prepared and submitted the following proposals and received funding as mentioned below:

1. In April 2011, Dr. Alam received funding from the Centre for Forest Science and Innovation (CFSI), Department of Natural Resources to produce bio-adsorbents from the cellulosic biomass **derived from forestry** for the recovery of precious metals.

2. In April 2011, Dr. Alam received a prestigious NSERC Discovery Grant for 3 years to conduct research for the recovery of gold from dilute solution using some biomass wastes.

3. Dr. Alam submitted a proposal to MMSB to produce bio-adsorbent using **biomass wastes derived from marine resources**. This proposal has been approved in August 2011.

4. In January 2012, Dr. Alam submitted a research proposal to the Harris Centre for the Harris Centre-MMSB Waste Management Fund (2012-2013) for the recycling of electronic waste. This project was awarded.

5. In February 01, 2012, Dr. Alam received NSERC-Engage Grant with Kruger Inc. for the recovery of gold using Kraft Mill lignin.

6. In March 01, 2012, Dr. Alam received NSERC-Engage Grant with Barrick Gold Corporation for the recovery of gold through biosorption.

As a result this Harris Centre-MMSB Waste Management Fund (2011-2012) helped to secure more funding from other sources and it became *a piece of a larger puzzle of this "Biomass NL" program for the management and proper utilization of solid biomass wastes.*

Budget Summary:

A "Statement of Account" for this Harris Centre/MMSB funded project is given below:

Statement of Account
Faculty of Engineering and Applied Science

Principal Investigator: Dr. S. Alam

Fund #: 207680 **Period Ending:** March 31, 2012

Title: Production of biomaterials from solid biomass wastes for the mining industry

Duration of Award: Feb 1, 2011-Mar 31, 2012 **Agency:** Harris Centre-MMSB Solid Waste Management

Total Award: $15,000.00
50% of funds released=$7500.00 upon approval
30% of funds released=$4500.00 at the midway point,
20% of funds released=$3000.00 upon recipt of final deliverables

Revenue		Not Received	Received
1st Installment - $7,500 Received July 19, 2011			$ 7,500.00
2nd Installment - $4,500 Received Nov 2, 2011			$ 4,500.00
3rd Installment - $3,000		$ 3,000.00	
	Total Available Funds for Year	**$ 3,000.00**	**$ 12,000.00**

Expenditures				
Date	Account	Description	Commitment	Actual
6-Apr-11	77012	GSS Stipend- M. Hossain, 16700pa, Apr1/11-Oct 31/11 stopped June 17/11		$ 4,881.55
28-Jun-11	77012	Expense tranferred to 207804 for M. Hossain		$ (3,596.93)
18-Aug-11	77012	Expense tranferred to 207804 for M. Hossain		$ (642.31)
9-Jun-11	70006	Shafiq Alam for items purchased-cartridge,projector screen, cables		$ 337.18
14-Jun-11	63030	WT Student Julie Kean-June 1/11-Sept 7, 2011		$ 8,653.41
15-Jul-11	76801	Lunch meeting re: Knowledge Mobilization		$ 19.95
9-Sep-11	77012	Expense tranferred to 207804 for M. Hossain		$ (642.31)
26-Sep-11	63030	WT Student Christina Blanchard - Sept 6/11 to Nov 30/11		$ 7,558.04
17-Oct-11	63030	Recovery 50% WT Julie Kean - (Yan Zhang - NSERC Discovery Grant)		$ (4,505.52)
4-Nov-11	78315	J/E - Poster Printer Usage Charge (July-Sep 2011)		$ 40.00
25-Oct-11	78315	J/E - ICP-OES Lab Charges, 2011 (M.Hossain)		$ 160.00
25-Oct-11	78315	J/E - ICP-OES Lab Charges, 2011 (M. Hossain)		$ 360.00
25-Oct-11	78315	J/E - ICP-OES Lab Charges, 2011 (M. Hossain)		$ 180.00
25-Oct-11	78315	J/E - ICP-OES Lab Charges, 2011 (M. Hossain)		$ 180.00
25-Oct-11	78315	J/E - ICP-OES Lab Charges, 2011 (M. Hossain)		$ 280.00
25-Oct-11	78315	J/E - ICP-OES Lab Charges, 2011 (M. Hossain)		$ 200.00
25-Oct-11	78315	J/E - ICP-OES Lab Charges, 2011 (O. Mehfuz)		$ 420.00
28-Mar-12	76801	Reimburse for Hosting Industry Personnel 2011-2012		$ 31.66
28-Mar-12	70302	Reimburse for minor computer purchases 2011-2012		$ 523.07
28-Mar-12	70006	Reimburse for materials and supplies 2011-2012		292.06
31-Mar-12	78315	ICP-OES Charges transferred from 207869 & 208267		$ 270.15
			$ -	$ 15,000.00
		Balance Available*		$ (3,000.00)

Notes:
*Available Balance takes into account commitments.
If you have any questions regarding this statement please see Marjorie Mercer

SECTION 2: RESEARCH DETAILS (PART – 1)

Production of Biomaterials (Bio-adsorbents) Using *Waste Cloth and Waste Paper* and Its Application for Gold Recovery

2.1 INTRODUCTION

Cellulose constitutes the most abundant and renewable polymer resource available worldwide. It is estimated that by photosynthesis, 10^{11}–10^{12} tons of cellulose are synthesised annually in a relatively pure form, for example, in the seed hairs of the cotton plant, but more often are combined with lignin and other polysaccharides (so-called hemicelluloses) in the cell wall of woody plants [1]. Cellulose has been used in the form of wood and cotton for thousands of years as an energy source, a building material and for clothing.

The molecular structure of cellulose as a carbohydrate polymer comprises of repeating β-d-glucopyranose units which are covalently linked through acetyl functions between the OH group of the C_4 and C_1 carbon atoms (β-1, 4-glucan). Cellulose is a large, linear-chain polymer with a large number of hydroxyl groups (three per anhydroglucose (AGU) unit) and present in the preferred $^4C_1$ conformation. To accommodate the preferred bond angles, every second AGU unit is rotated 180° in the plane. The length of the polymeric cellulose chain depends on the number of constituent AGU units (degree of polymerisation, DP) and varies with the origin and treatment of the cellulose raw material [1].

Literature search revealed that, in particular, two main approaches have been tried in the conversion of cellulose into compounds capable of adsorbing heavy metal ions from aqueous solutions. The first of these methods involves a direct modification of the cellulose backbone with the introduction of chelating or metal binding functionalities producing a range of heavy metal adsorbents. Alternative approaches have focused on grafting of selected monomers to the cellulose backbone either directly introducing metal binding capability or with subsequent functionalisation of these grafted polymer chains with known chelating moieties. Unmodified cellulose has a low heavy metal adsorption capacity as well as variable physical stability. Therefore, chemical modification of cellulose can be carried out to achieve adequate structural durability and efficient adsorption capacity for heavy metal ions [2]. Chemical modification can be used to vary certain properties of cellulose such as its hydrophilic or hydrophobic character, elasticity, water sorbency, adsorptive or ion exchange capability, resistance to microbiological attack and thermal resistance [3]. The dosage of a biosorbent strongly influences the extent of biosorption. An increase in the biomass concentration generally increases the amount of solute biosorbed. Due to increased surface area of the biosorbent which in turn increases the number of binding sites [4].On the other hand, the quantity of biosorbed solute per unit weight of biosorbent decreases with increasing biosorbent dosage which may be due to complex interaction of several factors. An important factor at high sorbent dosages is that the available solute is insufficient to completely cover the available exchangeable sites on the biosorbent, usually

resulting in low solute uptake [5]. Also, as suggested by Gadd et al. [6], the interference between binding sites due to increased biosorbent dosages cannot be overruled, as this will result in a low specific uptake.

In this project, investigation were done from preparing cellulose based bioadsorbent using waste cloth and shredded paper in a very simple way and using very low amount of chemicals. Experiments were done to observe the capacity, selectivity of the gels on gold or other precious metals adsorption. The factors which can affect the reaction by percentage, time or selectivity were also investigated. Kinetic studies of the reaction were observed by plotting different equations and try to find a good and acceptable result for both pilot and industrial scale.

References:

1. D. Klemm, H.P. Schmauder, T. Heinze, Cellulose, S. De Baets, E.J. Vandamme, A. Steinbuchel (Eds.), Polysaccharides II. Polysaccharides from Eukaryotes, Vol. 6, Wiley-VCH, Weinheim (2002), pp. 275–320.
2. S. Kamel, E.M. Hassan, M. El-Sakhawy, Preparation and application of acrylonitrile-grafted cyanoethyl cellulose for the removal of copper(II) ions. Journal of Applied Polymer Science, 100 (2006), pp. 329–334.
3. D.J. McDowall, B.S. Gupta, V.T. Stannett, Grafting of vinyl monomers to cellulose by ceric ion initiation. Progress in Polymer Science, 10 (1) (1984), pp. 1–50.
4. A. Esposito, F. Pagnanelli, A. Lodi, C. Solisio, F. Veglio, Biosorption of heavy metals by *Sphaerotilus natans*; an equilibrium study at different pH and biomass concentrations, Hydrometallurgy, 60 (2001), pp. 129–141.
5. J. Tangaromsuk, P. Pokethitiyook, M. Kruatrachue, E.S. Upatham, Cadmium biosorption by Sphingomonas paucimobilis biomass. Bioresource Technology, 85 (2002), pp. 103–105.
6. G.M. Gadd, C. White, L. DeRome, Heavy metal and radionuceotide uptake by fungi and yeasts.R. Norri, D.P. Kelly (Eds.), Biohydrometallurgy, Chippenham, Wilts, UK (1988).

2.2 MATERIALS AND METHODS

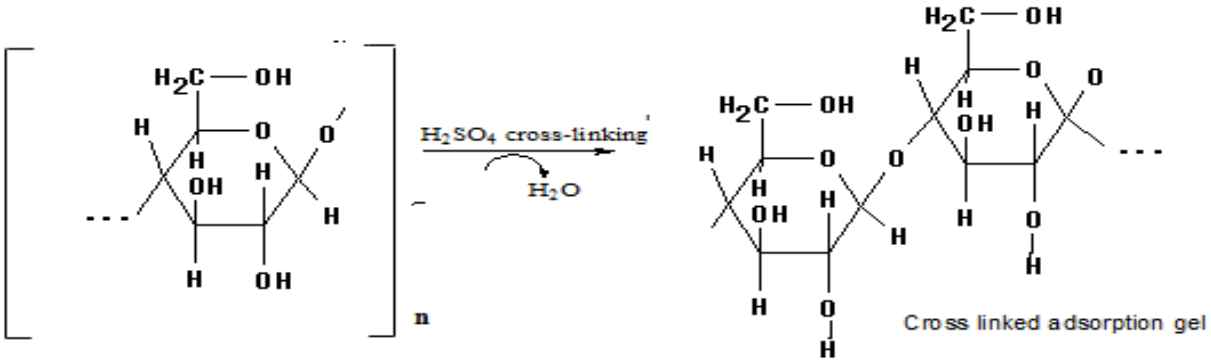
2.2.1 Materials

Analytical grade chloride salts of copper (Cu), iron (Fe), zinc (Zn), nickel (Ni), lead (Pb) and palladium (Pd) were used to prepare test solutions of respective metals. Analytical grade of gold [$HAuCl_4.4H_2O$] and platinum [$H_2PtCl_6.6H_2O$] were used to prepare gold and platinum solutions, respectively. All other chemicals used for the preparation of adsorbent and for adsorption tests were of analytical grade and were used without further purification.

2.2.2 Preparation of Adsorption Gel from Waste Cloth and Paper

As the raw material, daily used cloth and shredded paper were used in the present study to prepare cellulose gel (bio-adsorbent). For the preparation of the gel, 10 g of each thing was

suspended in 50 mL of concentrated sulfuric acid (18 M) in a round bottom flask and the mixture was stirred for 24 h at 373 K for cross-linking condensation reaction. After that, the mixture was cooled at room temperature and was neutralized with NaOH, followed by washing several times with distilled water until neutral pH. The black product obtained was dried in a convection oven for 24 h at 343 K. Then, the gel was passed through the 150 µm mesh size of testing sieve for regulating the uniform particles.



Scheme 2.1: Synthetic route of cross-linked adsorption gel.

2.2.3 Measurement and Analysis

The pH and concentration of metal solution were measured by using ORION 5STAR series pH meter, calibrated with buffers of pH 1.0, 2.0, 4.0 and 7.0 on a regular basis and a PerkinElmer optima Inductive Couple Plasma Optical Emission Spectrometer (ICPOES), respectively. Reproducibility of all adsorption experiments was confirmed by repeating the same adsorption test.

2.2.4 Batch Adsorption Test

In the present investigation, batch mode of operation was conducted in order to measure the adsorption behaviors of gold and other metal ions individually. Thus, in a representative experiment, 10 mg of dried gel was shaken together with 10 mL of each metal ion solution (0.2 mM) at varying hydrochloric acid concentration at 303 K for 24 h. After equilibrium, the mixture was filtered and the filtrate was analyzed for remaining metal ion concentration.

For the measurement of kinetics of adsorption, 200 mg of gel was mixed together with 200 mL of solution containing 0.2 mM of Au (III) in 1 M hydrochloric acid and stirred by using a magnetic stirrer at 298 K. Each 15 mL solution was sampled at definite time intervals from the start of the operation. Similar experiments were also carried out at 303, 313 and 323 K.

Adsorption isotherms of Au (III) were measured by shaking 10 mg (dry weight) of the gel in 10 mL solutions of 1 M hydrochloric acid varying the initial concentration of Au (III) in the range of 0.5-6 mM at four different temperatures (298, 303, 313 and 323 K) for 96 h. Percentage adsorption for each metal ion was calculated according to Eq. (1), where C_i and C_e (mM) represents the initial and equilibrium concentration, respectively. The amount of

adsorbed Au (III) (Q, mmol/g) was calculated by the mass balance calculation of Au (III) before and after the adsorption as expressed by Eq. (2)

$$\%A = \frac{Ci - Ce}{Ci} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$Q = \frac{C_i - C_e}{M} \times V \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

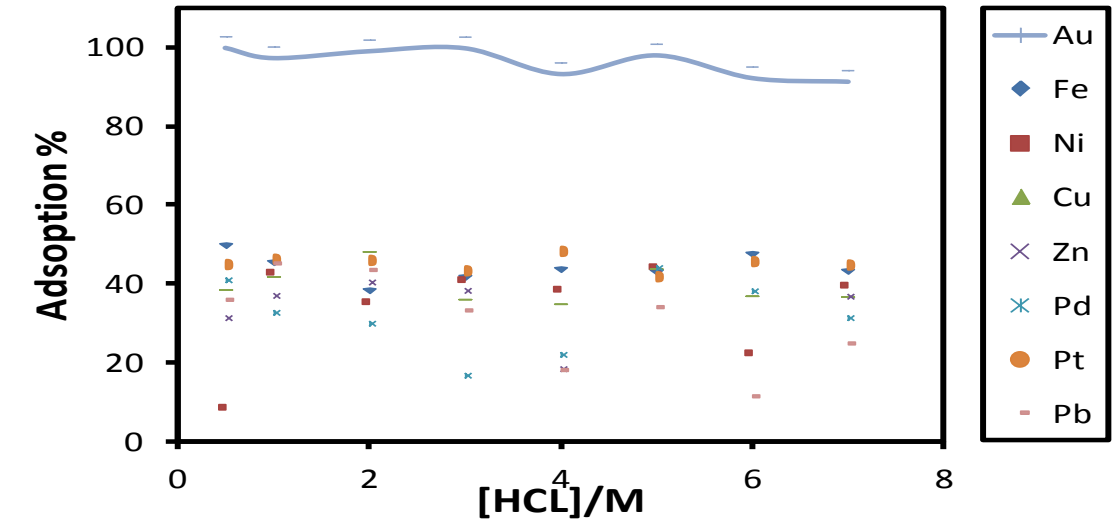
where, *V* (mL) is the volume of the test solution used and *W* (g) is the dry weight of the adsorbent.

For speed up the reaction time by increasing solid liquid ratio, 200, 1000 and 1600 mg of gel was mixed together with each 200 mL of solution containing 1 mM of Au (III) in 1 M hydrochloric acid and stirred by using a magnetic stirrer at 323 K. Each 15 mL solution was sampled at definite time intervals from the start of the operation.

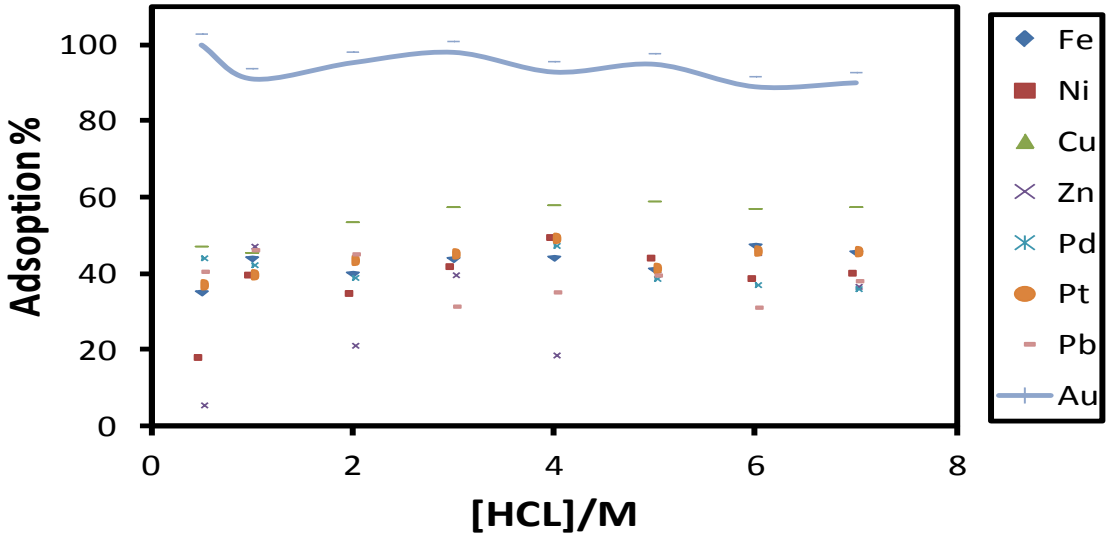
2.3 RESULTS AND DISCUSSIONS

2.3.1 Influence of pH for the Metal Adsorption

Figs. 2.3.1(a) and (b) show the adsorption of metals ions on cloth gel and paper gel, respectively, as a function of hydrochloric acid concentration. It is obvious from Fig. 2.3.1(a) and (b) that almost 100% adsorption of gold [Au(III)] was achieved in the low concentration range of hydrochloric acid while the extents of adsorption of other precious and base metals studied were very insignificant over the whole hydrochloric acid concentration regions. Thus, it is evident that both of the adsorption gel has a high affinity and selectivity for Au (III). From the viewpoint of selectivity and extent of Au (III) adsorption, the obtained result is quite interesting and it is expected to selectively recovery Au (III) separated from a number of other precious and base metals as tested in the present work.



(a)

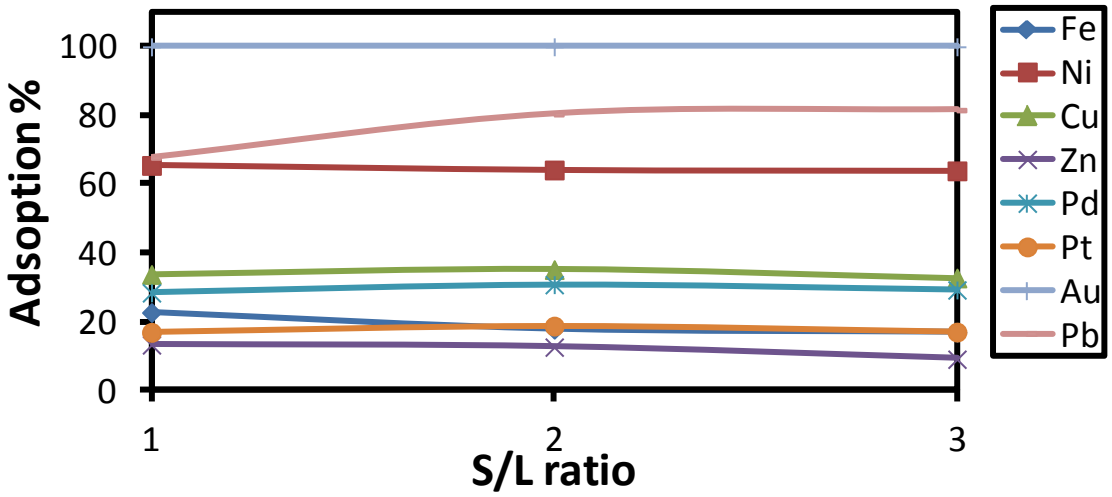


(b)

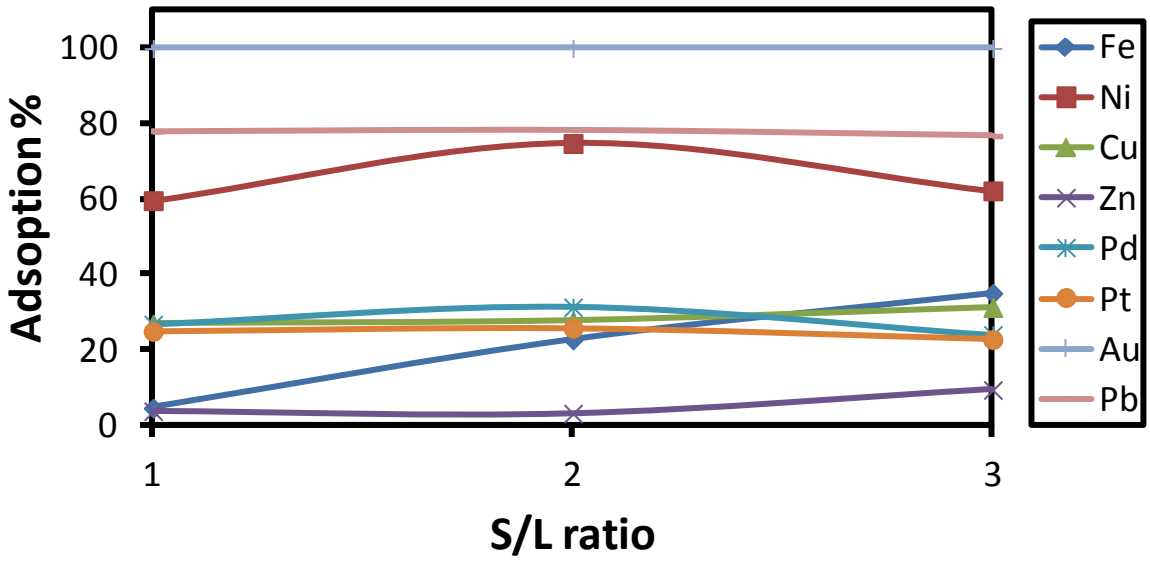
Fig. 2.3.1: Adsorption of metals ions on (a) cloth gel, (b) paper gel as a function of hydrochloric acid concentration. *Conditions*: weight of dry gel = 10 mg, volume of HCl solution = 10 mL, concentration of metals = 0.2 mM, shaking time = 24 h, temp = 303 K.

2.3.2 Effect of Solid/Liquid Ratio on Metal Adsorption

Figure 2.3.2 shows the effect of solid/liquid ratio on the adsorptive removal of the metal ions by the (a) cloth gel and (b) paper gel at the initial pH of 1. Adsorption does not change with the increases of solid liquid ratio.



(a)



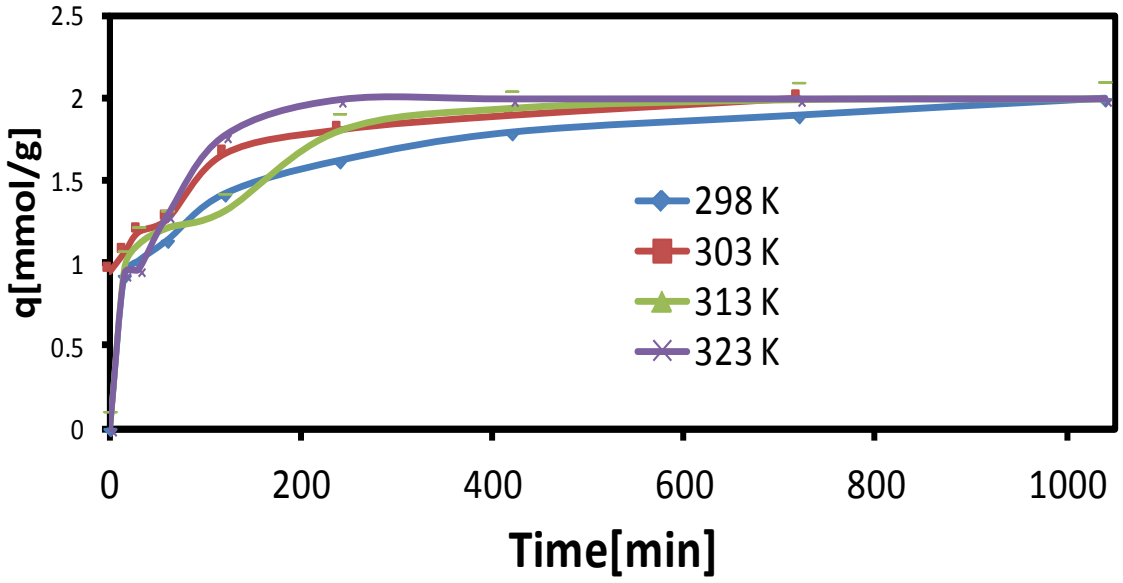
(b)

Fig. 2.3.2: Removal of metal ions from aqueous solution on the a) cloth gel, b) paper as a function of solid/liquid ratio.Weight of the gel = 20, 40, 60 mg. Initial pH = 3.5. Volume of the aqueous solution = 20 mL.

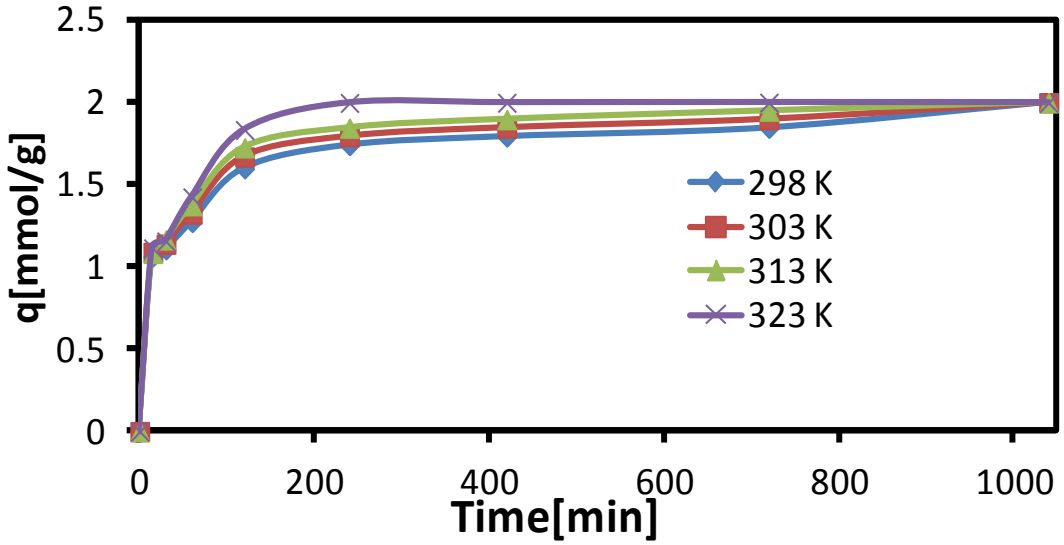
2.3.3 Adsorption Isotherms

As it was found that the gel is selective only for Au (III) ions, further experimental works were carried out only for Au (III) ions. The data of adsorption kinetics of Au (III) is illustrated in Figure 2.3.3. Figure 2.3.3 (a) for cloth gel and (b) for paper gel shows the variation of the amount of Au (III) adsorbed on the gel as the function of shaking time at different temperature. It is observed from this figure that temperature has a significant effect on the adsorption rate of Au (III). The time required to reach adsorption equilibrium is shortened

with increasing temperature. Furthermore, it is seen that the adsorption rapidly increases at the initial stages and then the adsorption rate is slowed down to zero at the final stages for all the temperatures tested. Since the equilibrium is reached nearly within 240 min for all temperatures studied for the present gel, the contact time was fixed at 24 h in the following experiments in order to completely ensure the adsorption equilibrium.



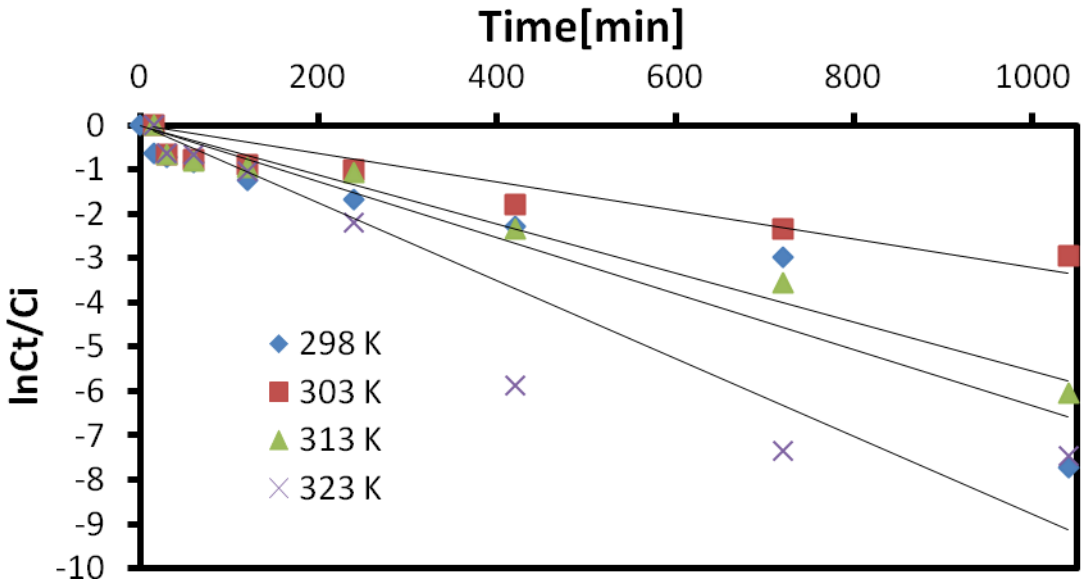
(a)



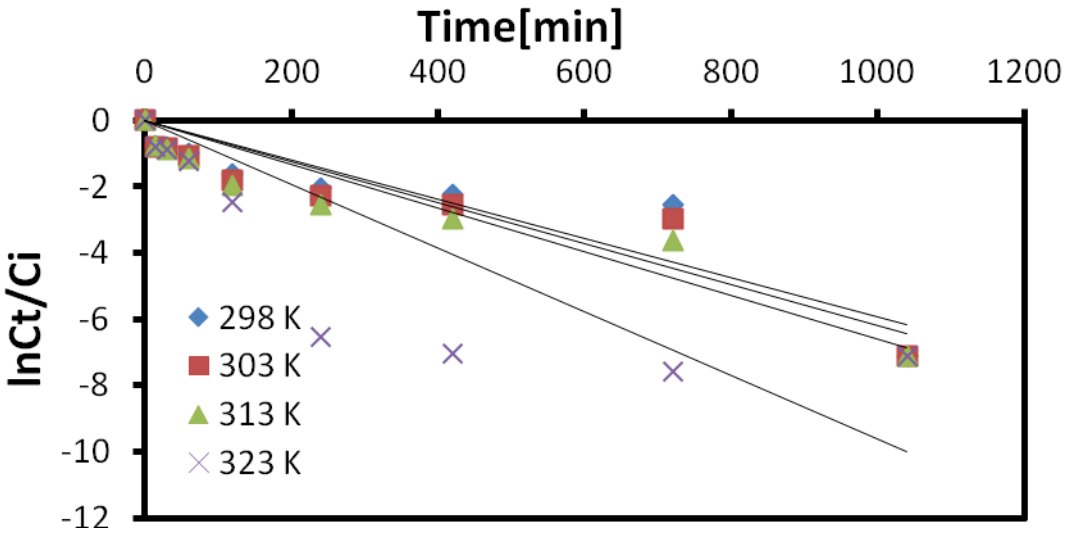
(b)

Fig. 2.3.3: Adsorption rate of Au (III) by the adsorption gel at different temperatures. *Conditions*: Weight of the dry gel = 200 mg, volume of the solution = 200 mL, concentration of Au (III) = 0.2 mM, HCl concentration = 1 M (a) on cloth gel and (b) on paper gel.

The kinetic data at the initial stage were re-plotted on the basis of the pseudo-first order kinetic model according to Eq. (3) as shown in Figure 2.3.4 (a) for cloth and (b) for paper. In this figure, nearly all plots appear to cluster on the straight lines passing through the origin corresponding to different temperatures. From the slopes of these straight lines, the pseudo-first order rate constants were evaluated at four different temperatures.



(a)



(b)

Fig. 2.3.4: Adsorption rate of Au (III) by the adsorption gel at different temperatures. Pseudo-first order plot *Conditions*: Weight of the dry gel = 200 mg, volume of the solution = 200 mL, concentration of Au (III) = 0.2 mM, HCl concentration = 1 M (a) on cloth gel and (b) on paper gel.

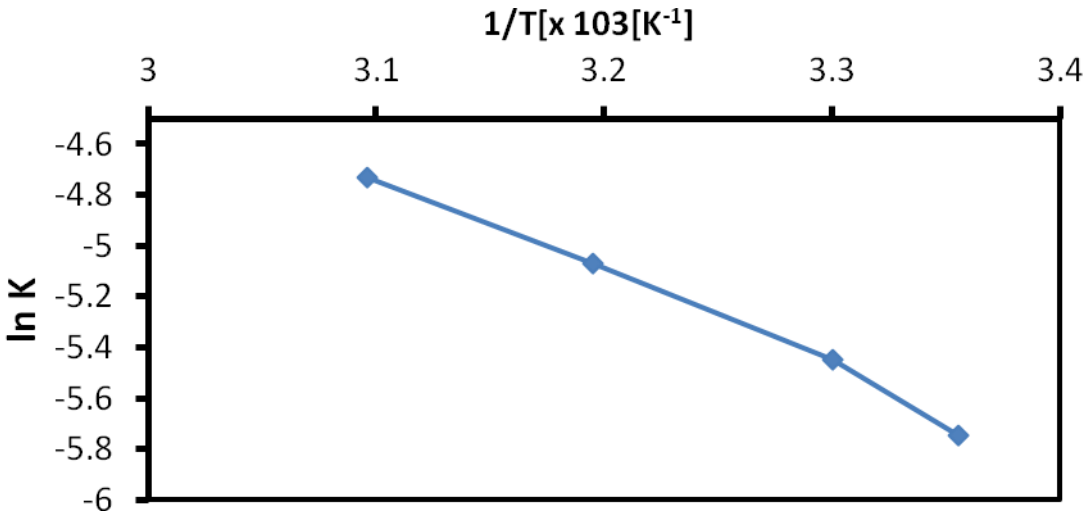
$$\ln (Ct/Ci) = - kt \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where, C_i and C_t (mM) represent the initial Au (III) concentration and the concentration at time, t, respectively, k represents the pseudo-first order rate constant (h^{-1}) and t is shaking time (h).

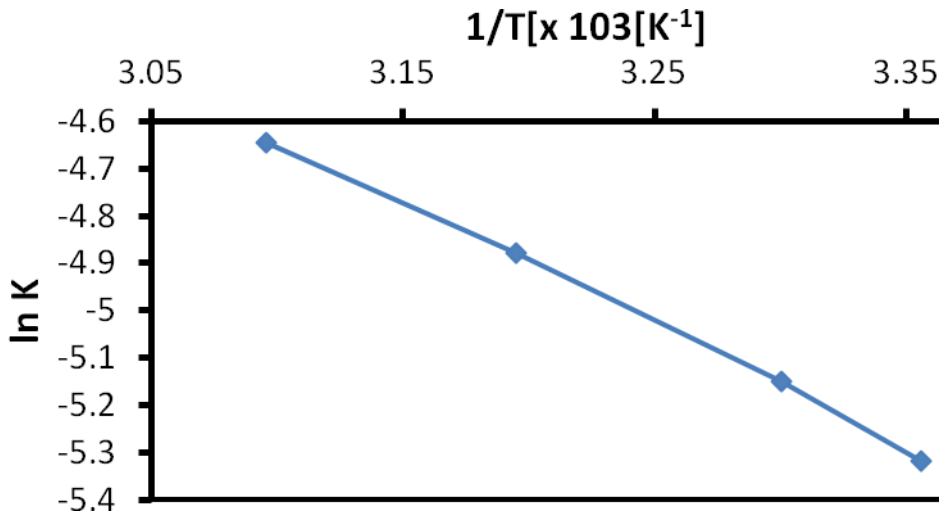
In order to evaluate the activation energy of the present adsorption reaction, the pseudo-first order rate constant evaluated at different temperatures were plotted in Figure 2.3.5 (a) for cloth gel and (b) for paper gel according to the Arrhenius equation as shown below:

$$\ln k = \ln A - Ea/RT \quad \ldots\ldots\ldots\ldots\ldots (4)$$

where, A represents the frequency factor, R is the universal gas constant, E_a is the activation energy (kJ mol^{-1}) and T is the absolute temperature (K).



(a)



(b)

Fig. 2.3.5: Adsorption rate of Au (III) by the adsorption gel at different temperatures. Arrhenius plot *Conditions*: Weight of the dry gel = 200 mg, volume of the solution = 200 mL, concentration of Au (III) = 0.2 mM, HCl concentration = 1 M (a) on cloth gel and (b) on paper gel.

Langmuir model is presented by the following equation:

$$q_e = q_m b C_e / (1+bC_e) \quad \ldots\ldots\ldots\ldots (6)$$

where, q_e and q_m are the equilibrium and maximum adsorption of metal ion per unit weight of adsorbent to form a complete monolayer on the surface bound at C_e, respectively; b is the equilibrium constant.

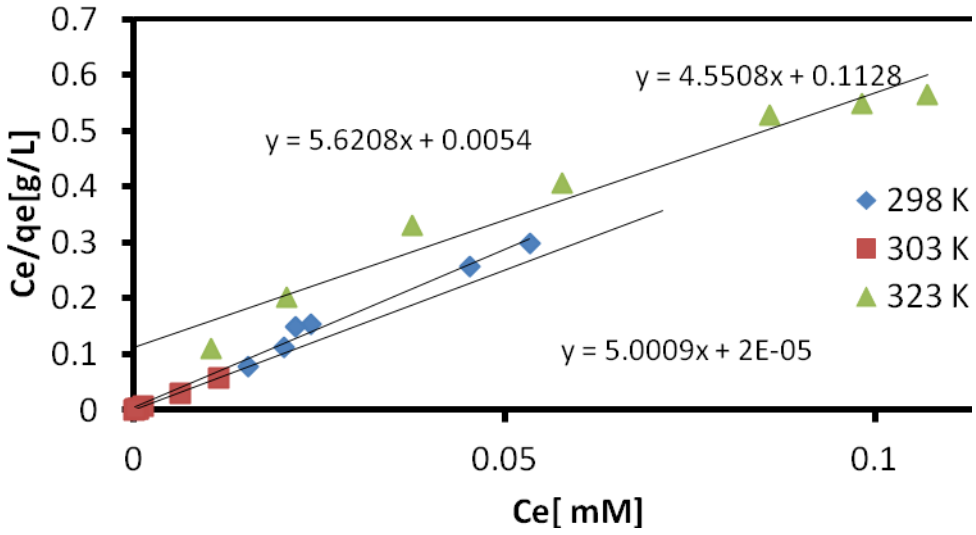
From the evaluated values of *b* at varying temperature, some thermodynamic parameters, such as, changes in the free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) associated to the adsorption process were evaluated according to the following equations.

$$\Delta G° = - RT \ln b \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

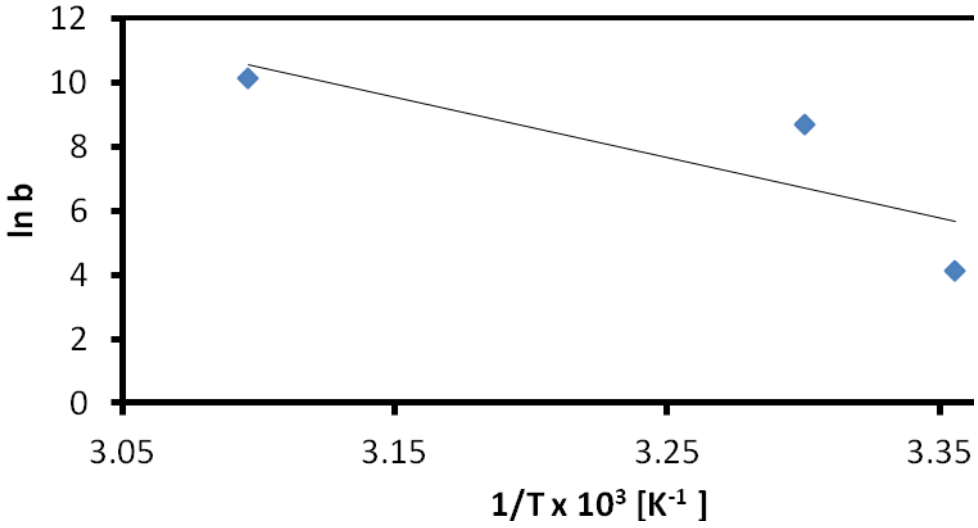
$$\ln b = - \Delta G°/RT = - \Delta H°/RT + \Delta S°/R \quad \ldots\ldots\ldots\ldots (8)$$

The plot ln*b* as a function of *1/T* as shown in Fig. 2.3.6 (for cloth) and Fig. 2.3.7 (for paper) yields a straight line with the correlation coefficient (r^2), from which the values of $\Delta H°$ and $\Delta S°$ can be calculated from the slope and intercept, respectively (Table 2.3.1). The more negative of $\Delta G°$, the stronger the driving force of the adsorption reaction. The decrease in the value of $\Delta G°$ with the increase of temperature shows that the reaction is more spontaneous at a high temperature which indicates that the adsorption processes are favored by the increase in temperature. Positive value of enthalpy ($\Delta H°$) demonstrates the endothermic nature of the adsorption. Entropy, as the measure of randomness of the

system, also indicates the positive values suggesting the increased mechanism of gold (III) adsorption.

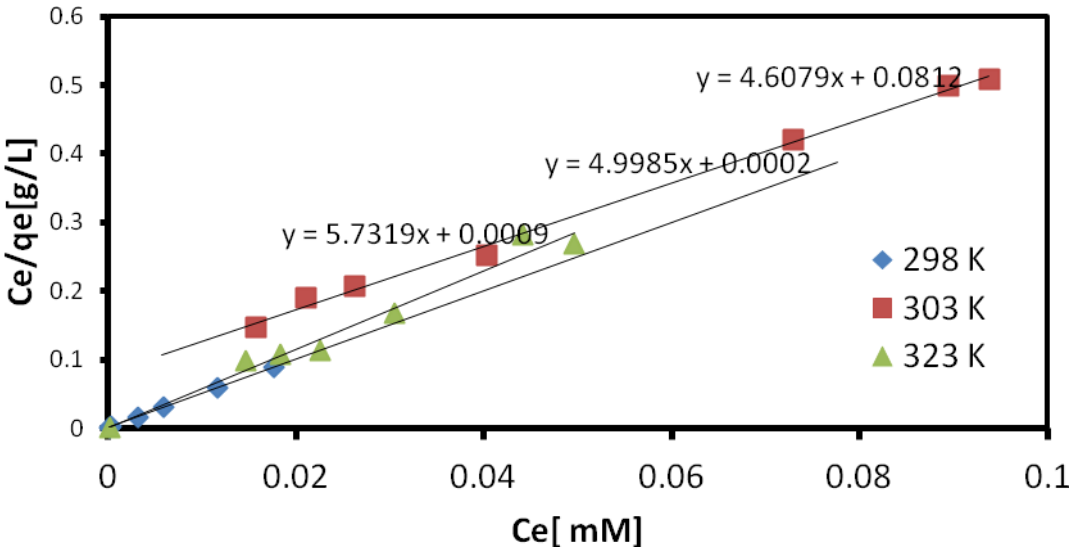


(a)

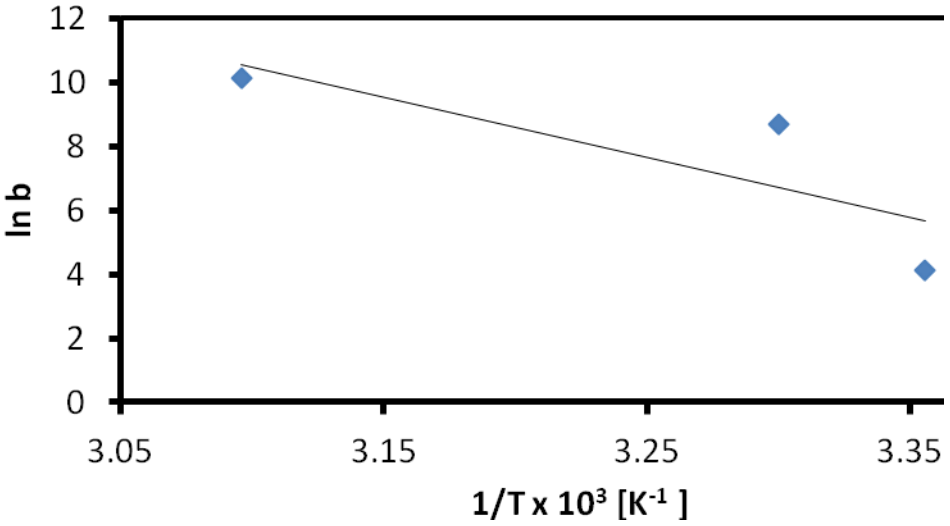


(b)

Fig. 2.3.6: Adsorption isotherms at different pH (a) Langmuir Plots (b) Van's Hoff plot for cloth gel.



(a)



(b)

Fig. 2.3.7: Adsorption isotherms at different pH (a) Langmuir Plots and (b) Van's Hoff plot for paper gel.

Table 2.3.1: Thermodynamic parameters for the adsorption of Au (III) on cross linked (a) cloth and (b) paper adsorbent gel.

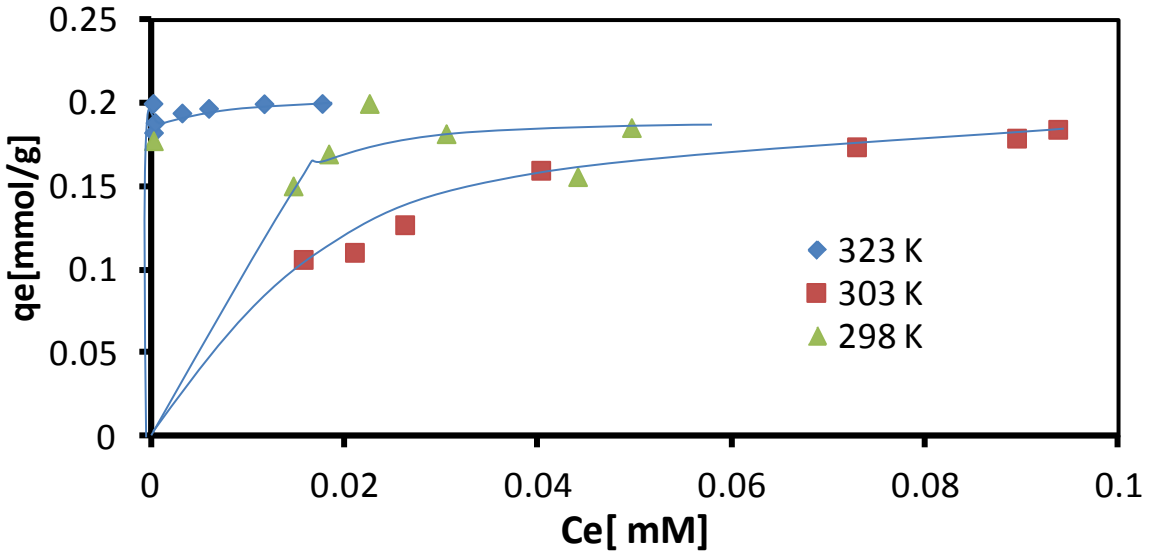
(a)

T.(K)	b L/mmol	lnb	q mmol/g	ΔG KJ/mol	ΔH KJ/mol	ΔS J/Kmol	R^2
298	44.34775	3.792062	1.9999	-18.148	-177.64	637.185	0.8278
313	1970.701	7.586145	1.999				
323	26359.91	10.1796	1.9999				

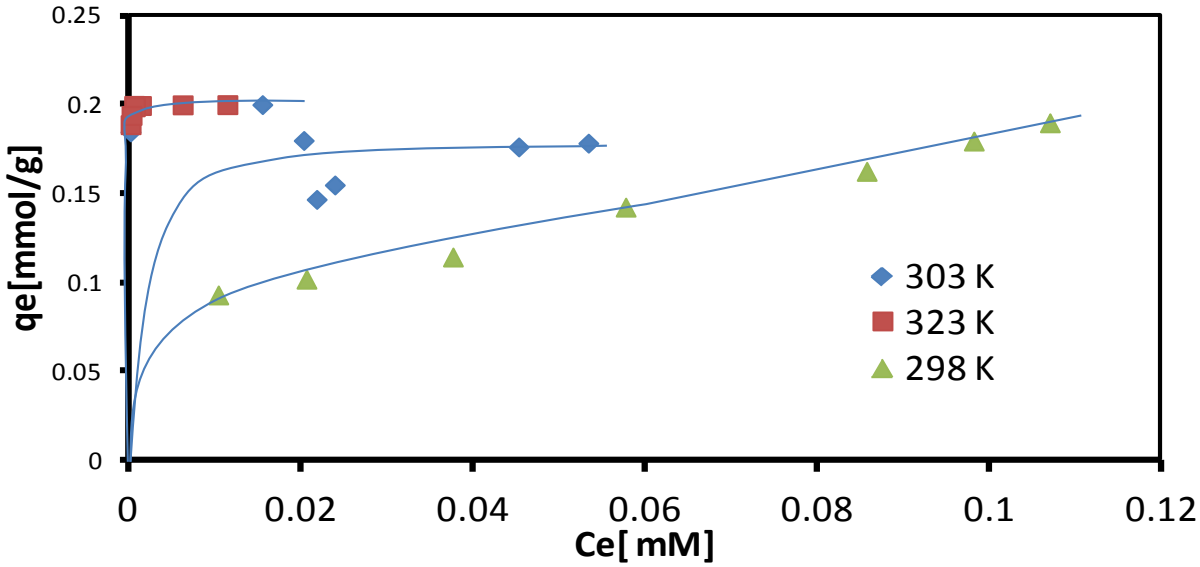
(b)

T.(K)	b L/mmol	lnb	q mmol/g	ΔG KJ/mol	ΔH KJ/mol	ΔS J/Kmol	R^2
298	61.68585	4.122055	1.9999	-19.36	-155.81	570.1242	0.6675
313	6028.491	8.704252	1.999				
323	25023.9	10.12759	1.9999				

The adsorption isotherms of Au (III) ions at various temperature are shown in Fig. 2.3.8 (a, b), where it was found that the gold adsorption capacity was increased with increasing equilibrium concentration of metal.



(a)

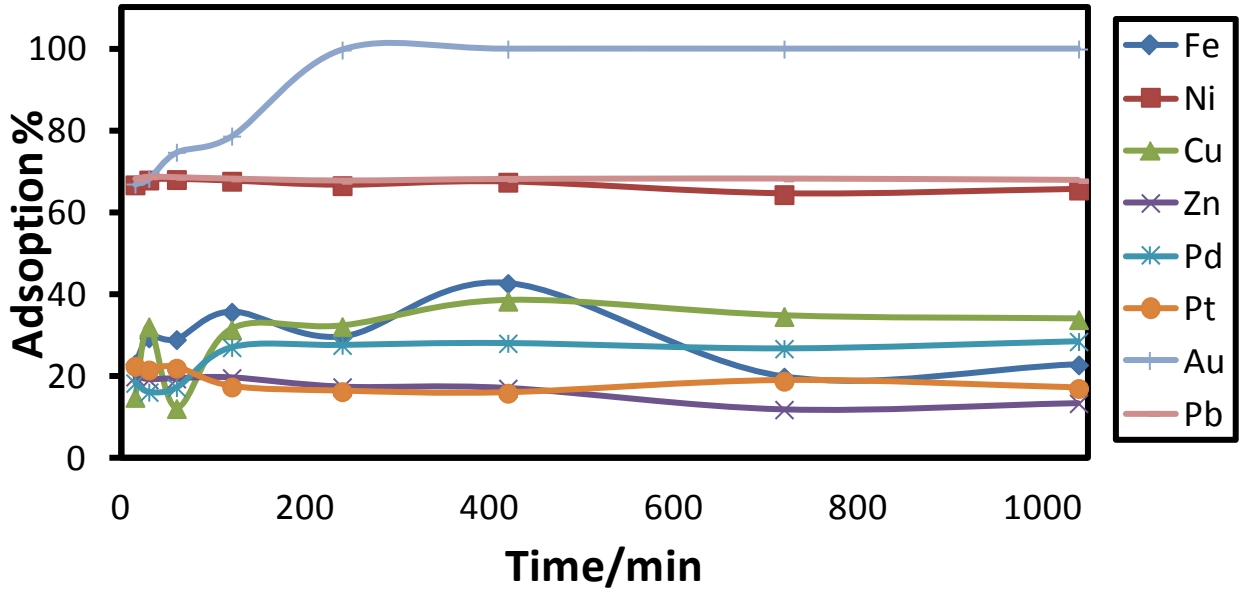


(b)

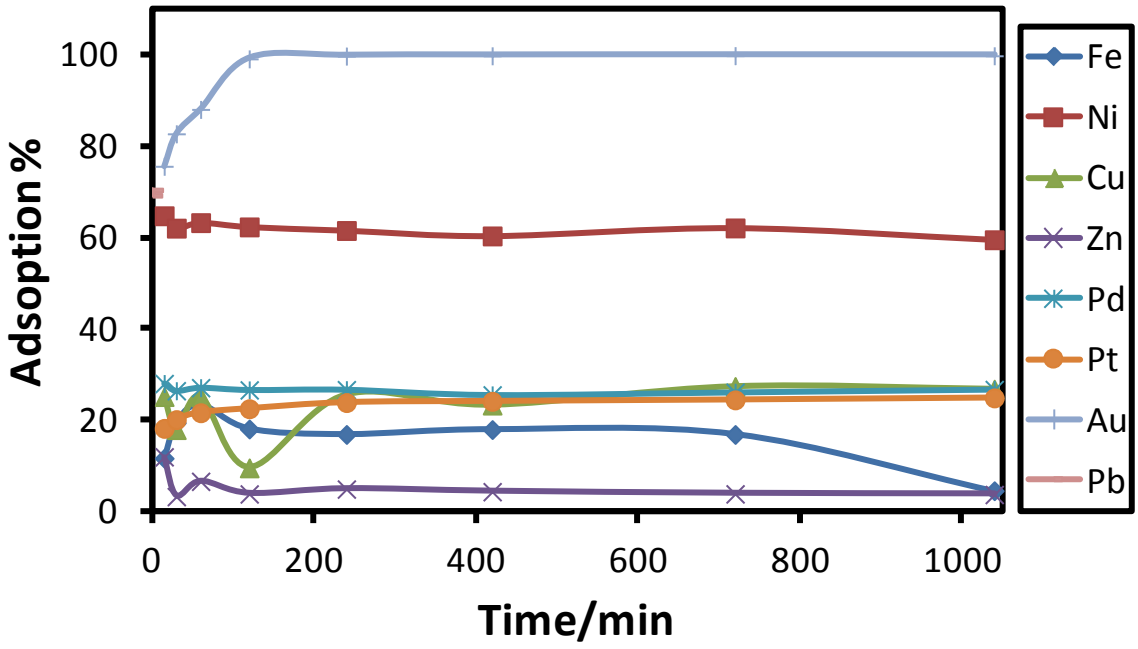
Fig. 2.3.8: Adsorption isotherms of Au (III) onto cellulosic gel at different temperatures. (a) For cloth and b) for paper. *Conditions*: weight of dry gel = 10 mg, volume of solution = 10 mL, shaking time = 24 h, HCl = 0.1 M.

2.3.4 Kinetic Studies

Figure 2.3.9 illustrates the evolution of metal uptake with time for two different gels. Adsorption occurs mainly within the first 240 min. Faster kinetics has significant practical importance as it will facilitate the scale up of the process to small reactor volumes, ensuring efficiency and economy. This behaviour is typical of biosorption of gold involving purely weak intermolecular forces between the biomass and the metal in solution.



(a)



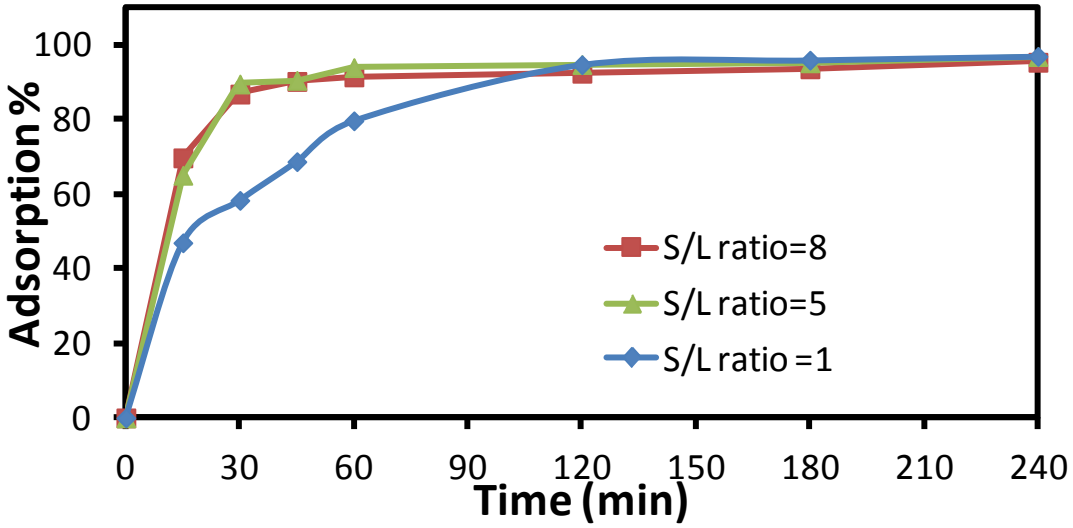
(b)

Fig. 2.3.9: Adsorption kinetics of different metal a) on cloth gel and (b) on paper gel

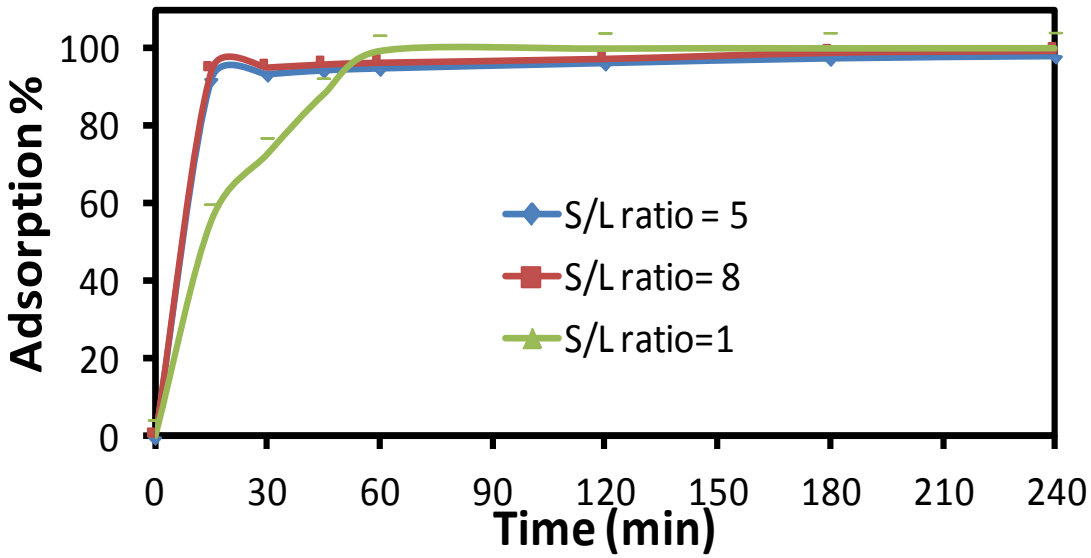
2.3.5 Effect of Increaing Solid/Liquid Ratio to Increase the Reaction Time

Figure 2.3.10 (a and b) shows the reaction kinetics at different solid-liquid (S/L) ratio for cloth and paper gel, respectively. In both cases when the solid liquid ratio is higer or equal

to five the reaction time are decreased considerably. Like for S/L ratio of 1 it took almost 120 min. to finish 90% of the adsorption, but for S/L ratio of 5 and 8 it happened only at first fifteen minutes which is acceptable at industrial range.



(a)



(b)

Fig. 2.3.10: Adsorption kinetics of different sample at different solid liquid (S/L) ratio. (a) on cloth gel, and (b) on paper gel.

As shown in Fig. 2.3.11, we also found higher gold adsorption capacity of 1.98 mol/kg and 1 mol/kg, respectively at 323 K for cloth and paper using higher solid liquid ratio.

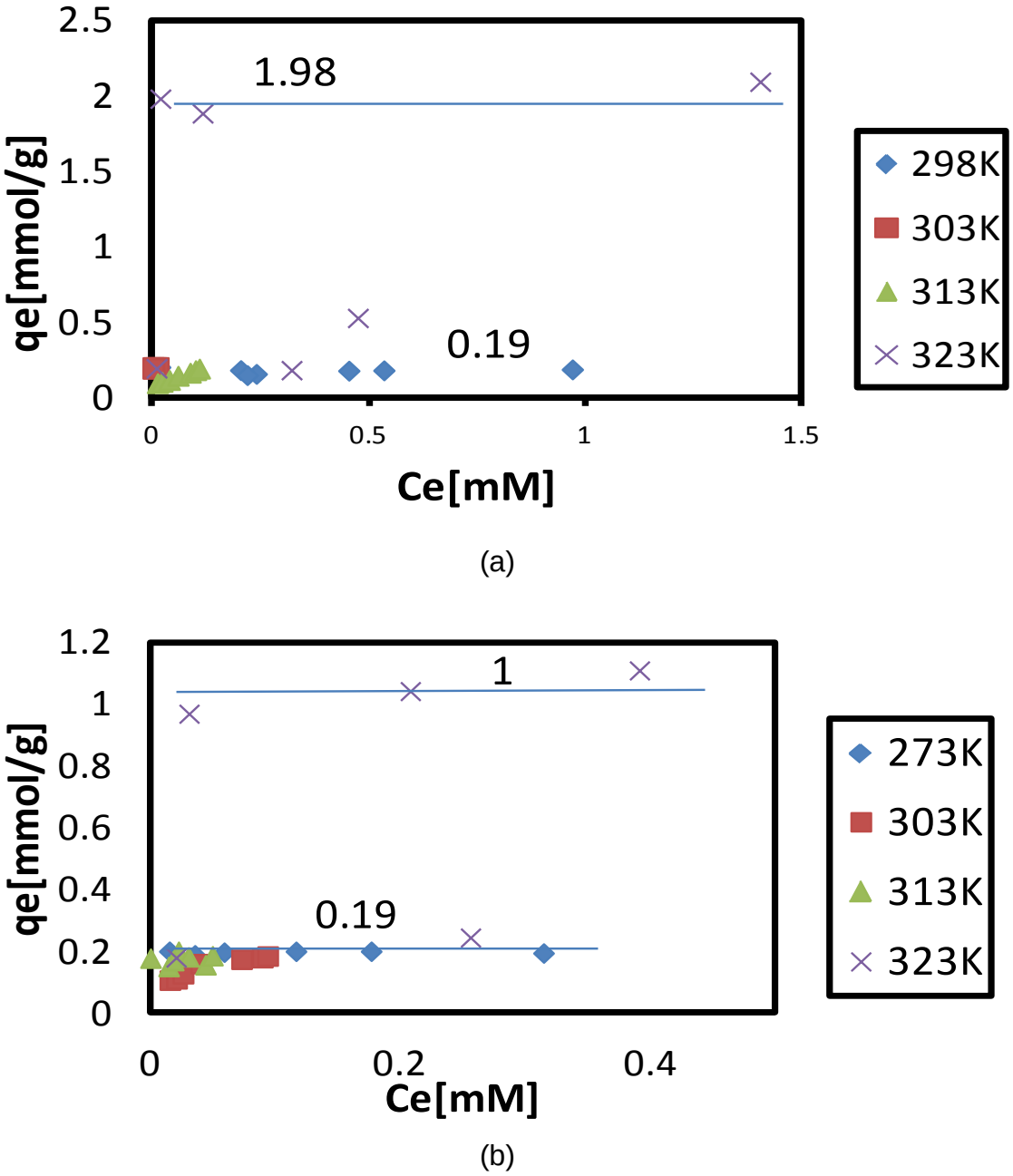


Fig. 2.3.11: Adsorption isothems of different sample at higher solid liquid ratio. (a) on cloth gel and (b) on paper gel.

2.3.6 Proposed Mechanism of Metal Adsorption

In this research it was found that gold [Au(III)] was strongly adsorbed on cloth and paper gel at pH 1-3, whereas it was poorly adsorbed at alkaline pH, suggesting the possibility of elution of metal using alkaline solution. Therefore, it is suggested that the adsorption mechanism of gold on cellulose gel is interpreted as shown in Fig. 2.3.12.

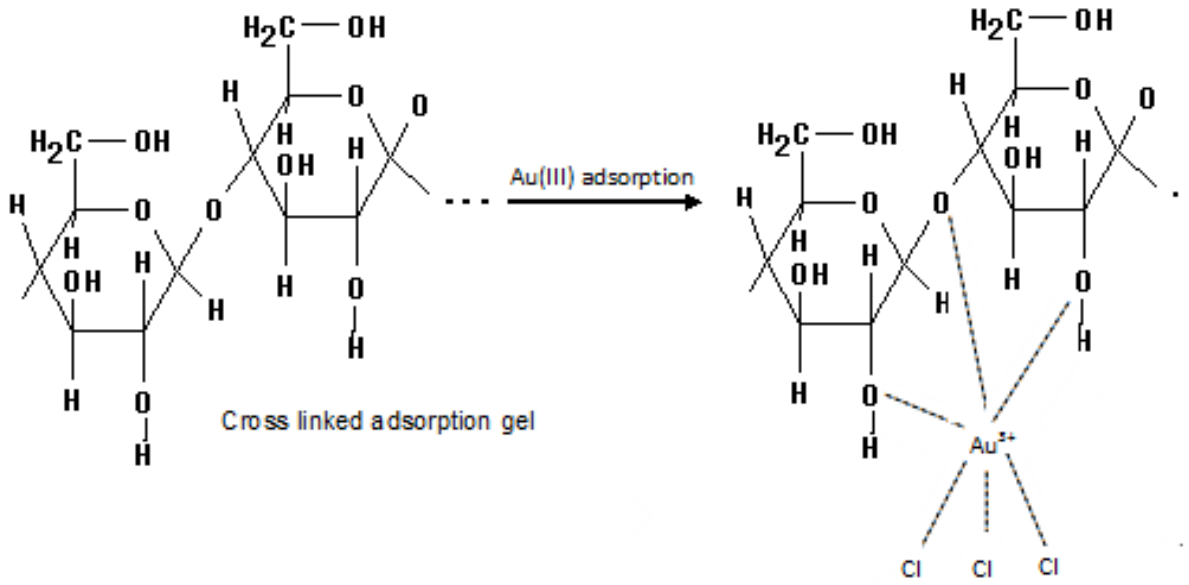


Fig. 2.3.12: Adsorption mechanism of Au(III) ions on cellulose based gel.

2.4 CONCLUSIONS

Biosorption of precious metals from solutions has received great deal of attention in the recent years. Compared with the conventional methods, a biosorption-based process offers a number of advantages including low operating costs, minimization of the volume of chemical and/or biological sludge to be handled and high efficiency in detoxifying effluents. Selective separation and recovery of gold away from any other precious or base metal ions can be achieved by using crosslinked cloth and paper gel. The excellent selectivity and high capacity of this gel provides a cost effective and environment friendly method for gold recovery. In this reaserch, the adsorption isotherm indicated clearly that the reaction product has an adsorptive capacity and was capable of recovering 388 g/kg gold. This adsorption follows a Type I process and fits the assumptions of the Langmuir isotherm. Kinetics data on the adsorbent determined that the gold uptake was very rapid, with maximum uptake occurring at approximately 240 min. These tests also demonstrated the dependence of the adsorption process on the initial concentration of gold in solution, with uptake rising with increased concentration. Further examination revealed a correlation of the process to the pseudo-second-order kinetics model. It was notable, however, that the overall rate constants and the initial sorption rates decreased as a result of higher initial concentrations of gold. The adsorption process was shown not to be affected significantly by temperature and the ideal pH of adsorption was found to be at pH 1-3. The 90% of the adsorption was achieved within first 15 min. by increasing in solid liquid ratio more than five times, which indicated its acceptability in industrial scale. These findings suggest that *cellulose based gel* prepared from waste cotton (cloth) and waste paper, exhibits significant potential as a bio-adsorbent for the recovery of gold from metallurgical solutions in mining industries.

SECTION 3: RESEARCH DETAILS (PART – 2)

Production of Biomaterials (Bio-adsorbents) Using *Waste Wood* and Its Application for Gold Recovery

3.1 INTRODUCTION

In this research cellulosic biomaterials (bio-adsorbents) were produced using solid biomass wood wastes which are abundantly available in this province. Wood samples (saw dust) were collected from seven different tree species including Black Spruce, White Birch, Yellow Birch, Eastern Birch, Red Pine, Balsam Fir, and White Spruce. These samples were used to make bio-adsorbents. Prepared bio-adsorbents were tested for the recovery of gold from aqueous metallurgical solutions in batch conditions.

3.2 MATERIALS AND METHODS

The wood saw dust was washed by de-ionized water and then dried in an oven at 70^{o}C for a period of 48 hours. The dried wood dusts were then treated with concentrated sulphuric acid (18 M) to enhance the dehydration-condensation reaction and activate cellulose sites. The treated wood dusts were washed and dried in an oven at 65^{o}C for a period of 24 hours, which were then ground and sieved to <150 micron. The sieved adsorbent was then used in the adsorption experiment. Synthetic aqueous solution (0.5 mM) of gold was prepared using reagent grade 1% w/v aqueous gold chloride ($HAuCl_4.3H_2O$) in a 2% nitric acid (HNO_3) media. Gold Chloride was supplied by Ricca Chemical Company. A 20 mL of synthetic gold chloride solution was taken in a 50 mL Erlenmeyer flask and 40 mg of adsorbents were added, which was then shaken in an air bath shaker at 300 rpm and 30^{o}C for a period of 68 hrs. At the end of shaking, the samples were filtered using Whatman No. 41 filter paper and the gold loaded adsorbents were separated. The concentrations of gold in the effluent were determined using Perkin Elmer ICP-OES (Perkin-Elmer Model Optima 5300 DV) and UV-Spectra. Calculations for gold concentration after adsorptions were done using feed concentrations and mass balance, then the adsorption efficiency was calculated.

Fig. 3.2.1: Generalized process flow for gold recovery.

a **b**

Fig. 3.2.2: a) Aqueous phase metal analysis using UV-Spectra, b) Air bath shaker (Innova-43 Incubator Shaker Series from New Brunswick Scientific) and oven.

3.3 RESULTS AND DISCUSSIONS

The adsorption efficiency (%) of the adsorbents prepared from seven different wood samples are presented in Fig. 3.3.1. This shows that almost 100% adsorption occurred for each of the samples.

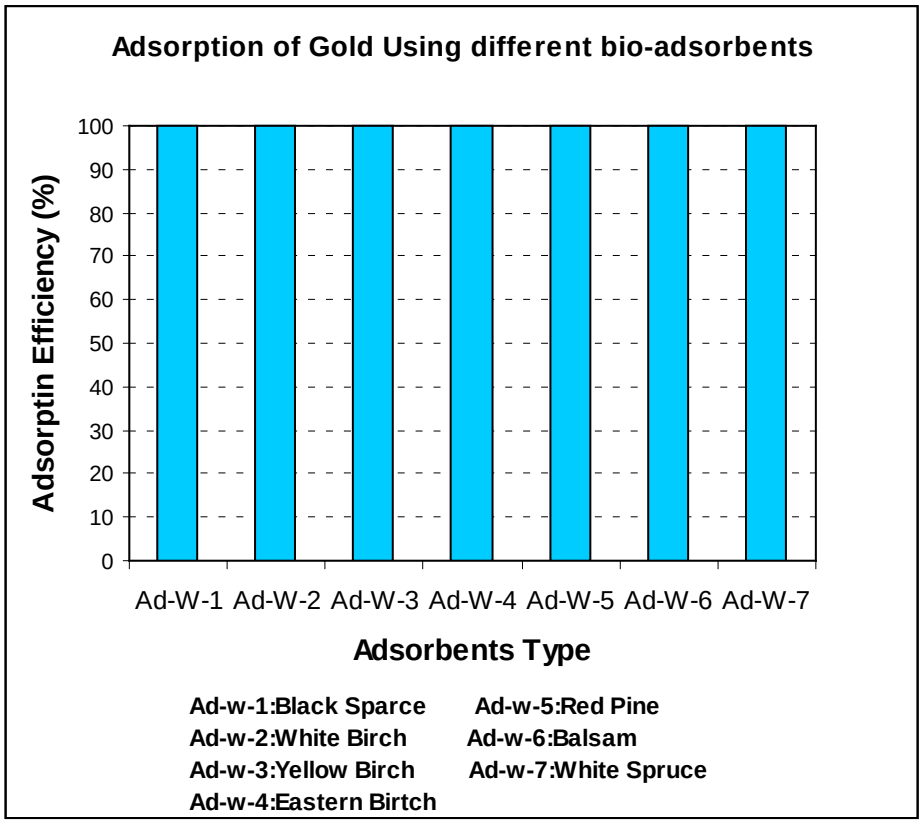


Fig. 3.3.1: Adsorption of gold using different bio-adsorbents prepared from wood dust. Feed solution: 0.5 mM, Temp.: 30^{o}C, S/L ratio: 2, Shaking speed: 300 rpm, Time: 68 hours.

Figure 3.3.2 shows the gold particle aggregates, which were visually observed.

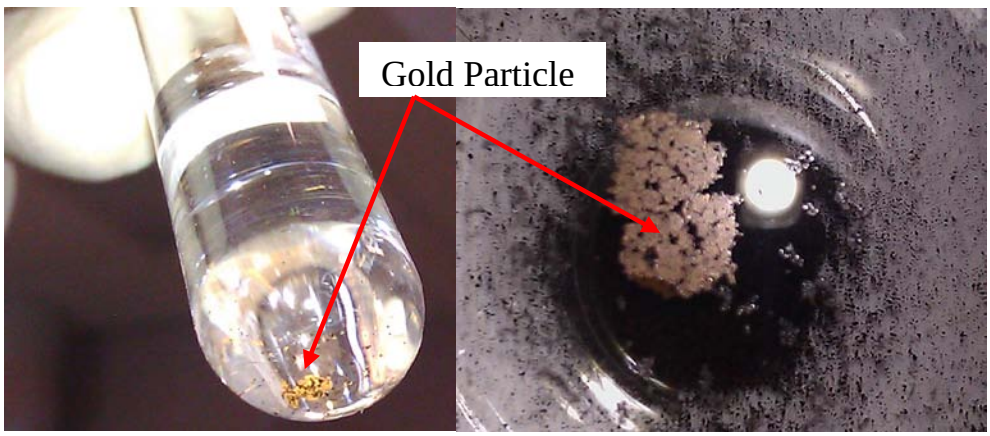


Fig. 3.3.2: Gold particle aggregates.

Figure 3.3.3 shows the adsorption mechanism of gold ions (Au^{3+}) with the functional group of cellulosic bio-adsorbent.

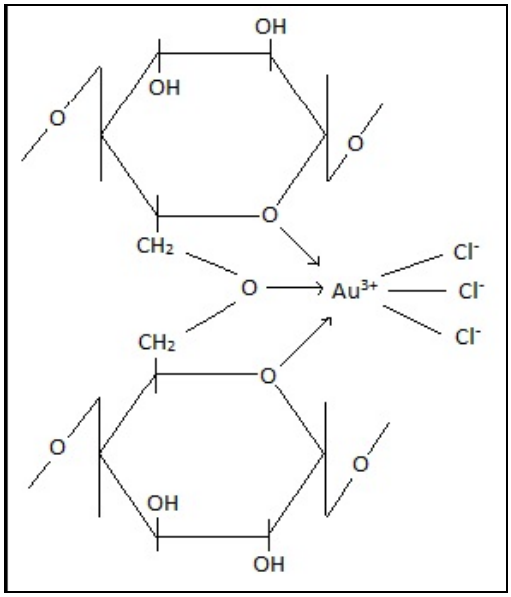


Fig. 3.3.3: Gold (Au) bonded with cellulosic bio-adsorbent.

The equilibrium isotherm was obtained by plotting the adsorption capacity (amount of gold adsorbed by the adsorbent in mg/mg) with equilibrium concentrations of gold. The percent adsorption (*A%*) and adsorption capacity (*q*) was calculated using the equations below:

$$A\% = [(C_i - C_e)/C_i] * 100$$

$$q = [(C_i - C_e)/W] x (L/1000)$$

where, C_i and C_e are the initial and equilibrium concentrations (mg/L) of gold, *W* is the mass of adsorbent(mg) and *L* is the aliquot of synthetic gold chloride solution in mL. As shown in Fig. 3.3.4, about 100% adsorption efficiency was achieved for the adsorbent prepared from red pine and black spruce for the concentration up to 800 mg/L of gold at a solid/liquid ratio of 2:1.

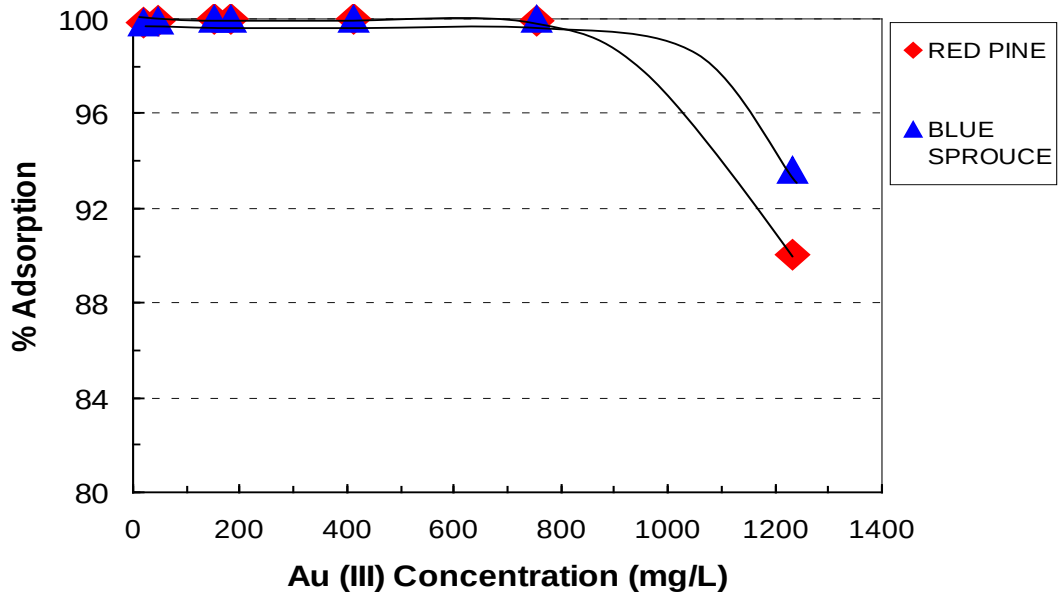


Fig. 3.3.4: Equilibrium adsorption isotherm for different concentrations of gold in aqueous phase.

Table 3.3.1 shows the adsorption and thermodynamic parameters of bio-adsorbents. The maximum adsorption (q_m) of Red Pine and Black Spruce was found to be 2.98 and 3.17 mol/Kg, respectively using a solid-liquid (S/L) ratio of 2 (mg/mL). For the fitting of experimental data, the linear regression was used as it can determine the best fitting isotherm and found that adsorption follows Langmuir Type-1 Isotherm as shown in the equation below:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K q_m}$$

Table 3.3.1: Adsorption parameters estimated from C_e/q_e vs.C_e Plot and $\Delta G^o = -RT \ln K_a$.

Parameters	Red Pine	Black Spruce
q_m (mol/Kg)	2.98	3.17
K_{ads} (L/gm)	0.128	0.120
R^2	0.9541	0.8802
ΔG^0 (KJ/mol-^{o}K)	- 5.178	- 5.341

Negative ΔG^0 indicates the feasibility or the spontaneous nature of the adsorption process and the value of the co-efficient of determination (R^2) indicates the strong evidence of Langmuir type-I adsorption isotherm

3.4 CONCLUSIONS

In this part of research, bio-adsorbents were prepared from the different waste wood / saw dust collected locally from St. John's, NL. The adsorption capacities of all the bio-adsorbents showed excellent performance. Using two types of prepared bio adsorbent (prepared from Red Pine and Black Spruce) it was found that 2.98 mol/Kg and 3.17 mol/Kg gold were adsorbed, respectively. It was observed that adsorption capacity was dominated by factors such as adsorbent dosage (solid-liquid ratio), pH of the solution, initial gold concentration, and time. The preparation of the bio-adsorbents was easy and simple. This process can be used to recover gold efficiently from an aqueous solution in an environmentally friendly manner. This research will drastically increase the value of waste wood for productive use in the mining industry. Both mining and waste management companies will benefit from this research.

APPENDIX – A
(Publications)

1. **M. Hossain**, ***S. Alam*** and W. Kelly, “Adsorption of Gold from Aqueous Solution Using Bio-adsorbent Prepared from Red Pine Wood Dust”, *Journal of Bioresource Technology* – (Manuscript prepared and is ready to submit).

— Journal of Bioresource Technology —

ADSORPTION OF GOLD FROM AQUEOUS SOLUTION USING BIO-ADSORBENT PREPARED FROM RED PINE WOOD DUST

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Abstract

This study investigated the adsorption of gold from an aqueous solution using an adsorbent prepared from the wood waste of native Red Pine wood (*Pinus resinosa*) collected from St. John's, Newfoundland, Canada. The effects of different parameters such as the initial gold concentration in aqueous solution, the initial solution pH, solid liquid ratio, and time of contact have been investigated in batchwise conditions. 100% adsorption efficiency of gold was achieved using this adsorbent, which was prepared through an easy and simple process. The feasibility study of the adsorbent was performed using the commonly used adsorption isotherm model of Langmuir and Freundlich, and the kinetics of gold (III) ion transport onto the adsorbent surface was also illustrated using a pseudo-first order model. It was found that a significant amount of the gold was adsorbed by the above mentioned adsorbent and could be used in the industries as an environmental friendly adsorbent.

Key words: Bio-adsorbent, Gold (III), Wood, Aqueous solution, Kinetics.

1. Introduction

The leach residue discarded in the mining industries often contains valuable metals like gold, silver, palladium in a lower concentration which are usually not feasible to extract by precipitation or solvent extraction method, used in the case of copper or nickel production. However, ion exchange or adsorption process is an alternative for extracting metal from the lower concentrated leach residue. Cellulosic bio-adsorbents have strong affinity to gold and can make the gold recovery process greener by replacing the chemical based precipitation or solvent extraction (SX) reagents.

In this study the use of cellulose based adsorbents, prepared from wood dust of red pine for the recovery of gold from an aqueous solution (e.g. leach residue), has been investigated in batch wise experimental conditions. The Red Pine solid biomass wood waste is abundantly available in Newfoundland and other parts of Canada. Red pine

2. **M. Hossain**, **S. Yao**, ***S. Alam*** and Y. Zhang, "Recovery of Gold from Aqueous Solution using Bio-adsorbent Prepared from Wood Waste", *Proceedings of the 50th Annual Conference of Metallurgists (COM2011)* held in conjunction with World Gold, Poster Presentation, October 2-5, Montreal, QC, Canada (2011).

Recovery of Gold from Aqueous Solution Using Bio-Adsorbent Prepared from Wood Waste

COM 2011 — CONFERENCE OF METALLURGISTS — MONTREAL, QC

Mirza Hossain, Shuaihong Yao, Shafiq Alam, Yan Zhang
Faculty of Engineering and Applied Science, Memorial University of Newfoundland

Background and Introduction

- The purpose of this study was to develop a simple, environmentally friendly, and low cost process for the recovery of gold.
- Conventional gold recovery processes often are more complex, expensive, less efficient, and have negative environmental impacts.
- Currently activated carbon is used in the industry, however it is not selective to gold as it co-adsorbs other metals. Also, removal of gold from the carbon is very difficult because gold is trapped inside the micro-pores of the carbon particles.
- This research focuses on the extraction of gold using cellulosic bio-adsorbents derived from solid biomass wood waste.
- Wood samples (saw dust) were collected from seven different tree species including Black Spruce, White Birch, Yellow Birch, Eastern Birch, Red Pine, Balsam Fir, and White Spruce. These samples were used to make bio-adsorbents.
- The gold adsorption capacities of the bio-adsorbents, prepared from the wood dust received locally from St. John's, Newfoundland, were excellent.

Procedure

- The wood saw dust was washed by de-ionized water and then dried in an oven at 70°C for a period of 48 hours.
- The dried wood dusts were then treated with concentrated sulphuric acid to enhance the dehydration-condensation reaction and activate cellulose sites.
- The treated wood dusts were washed and dried in an oven at 65°C for a period of 24 hours, which were then ground and sieved to <150 micron.

Fig. 1. Generalized Process Flow for Gold Recovery

- Synthetic aqueous solutions of gold at different concentrations were prepared using reagent grade gold chloride solution.
- A 20 mL of synthetic gold chloride solution was taken in a 50 mL Erlenmeyer flask and 40 mg of adsorbents were added, which was then shaken in an air bath shaker at 300 rpm and 30°C for a period of 68 hrs.
- At the end of shaking, the samples were filtered and the gold loaded adsorbents were separated.

Results and Analyses

- The adsorption efficiency (%) of the adsorbents prepared from seven different wood samples are presented in Fig.2. This shows that almost 100% adsorption occurred for each of the samples.

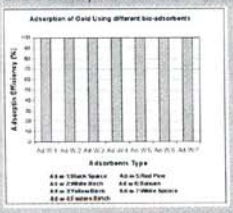

Fig.2. (on left) Adsorption of Gold Using Different Bio-adsorbents Prepared from Wood Dust.

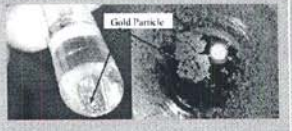

Fig.3. (on right) Gold Particle Aggregates Which can be Visually Observed.

- The adsorption of gold was initially confirmed by the UV-spectra as shown in Fig.4.

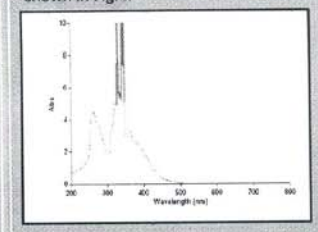

Fig.4. UV Spectra

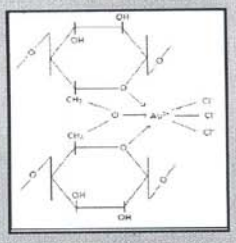

Fig.5. Gold (Au) Bonded with Cellulose

- The concentrations of gold in the effluent were determined using Perkin Elmer ICP-OES. Calculations for gold concentration after adsorptions were done using feed concentrations and mass balance, then the adsorption efficiency was calculated.
- The equilibrium isotherm was obtained by plotting the adsorption capacity with equilibrium concentrations.

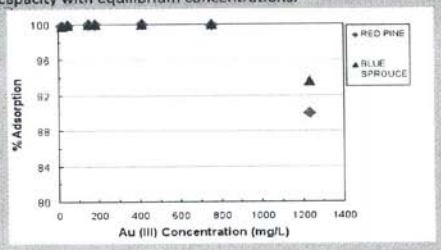

Fig.6. (on left) Concentration vs. Adsorption

Table 1. (below) Estimated Adsorption Parameters

- Equations used include:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{Kq_m}$$

$$A\% = [(C_i - C_e)/C_i] * 100$$

$$q = [(C_i - C_e)/W]x(L/1000)$$

Parameters	Red Pine	Black Spruce
q_m (mole/Kg)	2.98	3.17
K_{ads} (L/gm)	0.128	0.120
R^2	0.9541	0.8802
ΔG^0 (KJ/mol-°K)	- 5.178	- 5.341

- About 100% adsorption efficiency was achieved for the adsorbent prepared from red pine and black spruce for the concentration up to 800 mg/L of gold at a solid/liquid ratio of 2:1.

Conclusions

- The adsorption capacities of all the samples of bio-adsorbent prepared from the different wood dust showed excellent performance.
- Using two types of prepared bio adsorbent (prepared from Red pine and Black spruce) it was found that 2.81 mol/Kg and 2.91 mol/Kg gold were adsorbed, respectively.
- It was observed that adsorption capacity was dominated by factors such as adsorbent dosage (solid-liquid ratio), pH of the solution, initial gold concentration, and time.
- The preparation of the bio-adsorbents was easy and simple. This process can be used to recover gold efficiently from an aqueous solution in an environmentally friendly manner.
- This research will drastically increase the value of wood for productive use in the mining industry. Both mining and forest industries will benefit from this research.

Acknowledgments

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3. B. Pangeni, H. Paudyal, M. Abe, **K. Inoue**, H. Kawakita, K. Ohto, B.B. Adhikari and ***S. Alam***, "Selective Recovery of Gold Using Some Cross Linked Polysaccharide Gels", *Green Chemistry*, The Royal Society of Chemistry Journals, – Article in Press (Accepted on April 10, 2012),

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Selective recovery of gold using some cross linked polysaccharide gels

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Abstract

Effective recovery of gold from aqueous acidic chloride media was found to be achieved with different kinds of polysaccharides with different structures by treating with concentrated sulfuric acid. The gels were found to be highly selective for Au(III) over other precious and base metals at varying hydrochloric acid solution. The adsorption isotherms of Au(III) followed the Langmuir type of adsorption and the maximum adsorption capacities for Au(III) was evaluated as high as 7.57, 7.20, 5.64 and 4.80 $mmol.g^{-1}$ for the gels of cellulose, dextran, alginic acid and pectic acid, respectively. Analysis of kinetic data shows that the uptake of gold(III) at initial stage follows the pseudo-first order kinetics for cellulose gel. Crystalline structure of the cellulose before and after the treatment with concentrated sulfuric acid was measured by XRD-analysis. Furthermore, Au(III) was found to be reduced to elemental form by all types of polysaccharides gels, which was confirmed by the formation of clearly visible elemental gold particles and by means of the XRD-spectrum of the adsorbents after the adsorption. Infrared spectrum studies provided the supporting evidences for the reduction of Au(III) to Au(0) with the suitable mechanism of Au(III) adsorption followed by reduction using various polysaccharide gels.

Keywords: Polysaccharide, Sulfuric acid treatment, Au(III), Adsorption, Elemental gold

4. B. Pangeni, H. Paudyal, **K. Inoue**, H. Kawakita, K. Ohto and ***S. Alam***, "An Assessment of Gold Recovery Processes Using Cross-Linked Paper Gel", *Journal of Chemical & Engineering Data*, American Chemical Society (ACS) Publications, 57, 796−804 (2012).

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Article

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An Assessment of Gold Recovery Processes Using Cross-Linked Paper Gel

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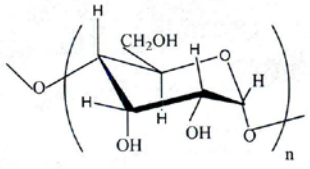
ABSTRACT: A novel type of adsorption gel was prepared from filter paper by treating it with concentrated sulfuric acid to investigate the efficient adsorption of Au(III) from aqueous acidic chloride media. Various parameters have been examined for the recovery of gold such as effects of hydrochloric acid concentrations, contact time, initial Au(III) concentrations, and temperature. The adsorption of gold was fitted with the Langmuir type adsorption model, and the maximum adsorption capacity of gold was evaluated as 5.05 mmol·g^{-1}. The kinetics of gold adsorption was interpreted in terms of the pseudofirst-order kinetic model, and the activation energy was evaluated as 61.3 kJ·mol^{-1}. The gold adsorbed by the paper gel was measured by means of X-ray diffraction spectrum, scanning electron microscope (SEM), and an optical microscope. The inferred mechanism for the adsorption of Au(III), followed by its reduction to elemental gold, was proposed based on the observation of infrared spectroscopic analysis. It was inferred that Au(III) was adsorbed by the coordination to oxygen atom of C−O−C linkage formed after the cross-linking with concentrated sulfuric acid, as well as the oxygen atoms of hydroxyl groups of pyranose rings of paper cellulose. The adsorbed gold can easily be recovered by the incineration method at elevated temperature.



1. INTRODUCTION

During the past decade, with the development of consumer-oriented electrical and electronic technologies, large amounts of electronic equipment have been provided to the market. The useful life of these devices is relatively short and has been decreasing as a result of rapid changes in equipment features and capabilities. The short useful life of these products brings about a large waste stream of obsolete electronic and electrical devices (e-waste).

Precious metals have a wide variety of applications in the manufacturing of electronic appliances, serving as contact materials due to their high chemical stability and good conducting properties.[1] Gold recovery from secondary sources such as electronic scraps and waste electroplating solutions is, therefore, remarkable technology.[2] Several studies reported that recovering precious metals from electronic scraps is one of the greatest economic profits for the recycling industry. The disposal e-wastes contain a higher proportion of precious metals than in the ore itself. Additionally, the purity of precious metals like gold in the printed circuit board (PCB) in e-waste is more than 10 times that of the corresponding minerals.[3]

Presently, many processes such as solvent extraction,[4] ion exchange,[5] and coprecipitation[6] have been available to separate and enrich the gold. However, these processes are only feasible for specially processed solutions containing high gold concentrations. These processes also suffer from various problems like low yields, operational difficulties, and environmental concerns. On the other hand, adsorptive separation, which is an efficient recovery process for gold from dilute solutions, also suffers from some problems such as insufficient selectivity. This gives a compelling reason for developing more efficient and more environmentally friendly methods for the recovery of precious metals, not only from mineral ores but also from waste materials such as e-waste.[7]

Bioadsorption is expected to be a promising technique for metal recovery since biomasses not only exhibit interesting adsorption behaviors for metal ions but also are environmentally friendly, biodegradable, and biocompatible. Therefore, they have attracted significant attention in recent years.

Cellulose, a polysaccharide made by most plants, is one of the most abundant organic compounds on earth. The chemical modification of polysaccharides is the most important route to modify the properties of the naturally occurring biopolymers, including cellulose, and to use this renewable resource in the context of sustainable development. This is because the hydroxyl groups in cellulose can coordinate with metal ions to form stable complexes.

In our previous studies, we had developed different kinds of adsorption gels for recovering precious metals such as dimethylamine-immobilized (DMA) paper gel, *p*-aminobenzoic (PAB) acid modified paper gel, and iminodiacetic acid (IDA) type of modified waste paper gel[8−10] from waste paper. These adsorption gels exhibited the maximum adsorption capacity for Au(III) as high as (4.6, 5.09, and 3.30) mmol·g^{-1} by DMA, PAB, and IDA type of modified waste paper gel, respectively. However, high costs are associated with the preparation of

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5. B. Pangeni, H. Paudyal, **K. Inoue**, H. Kawakita, K. Ohto and ***S. Alam***, "Selective Recovery of Gold(III) Using Cotton Cellulose Treated with Concentrated Sulfuric Acid", *Cellulose*, DOI 10.1007/s10570-011-9628-6 (2011).

Selective recovery of gold(III) using cotton cellulose treated with concentrated sulfuric acid

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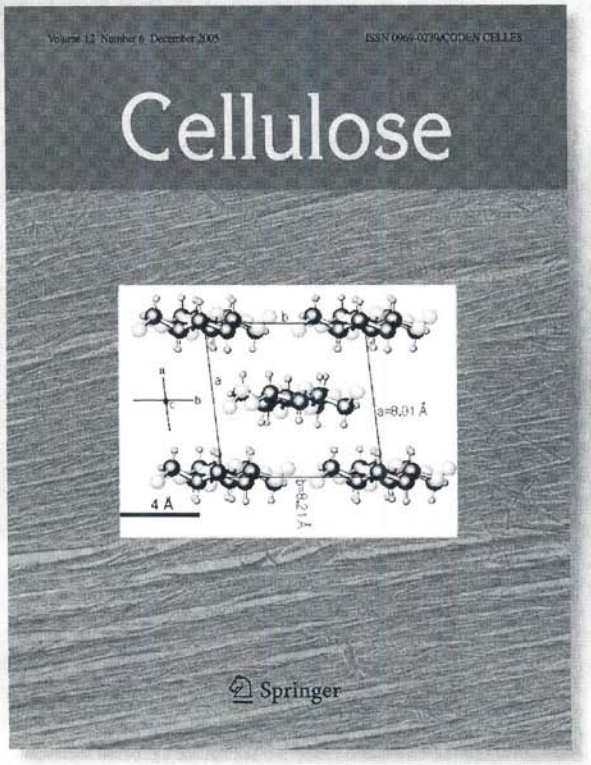

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Selective recovery of gold(III) using cotton cellulose treated with concentrated sulfuric acid

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Abstract Novel utilization of cotton cellulose was developed by chemically modifying with concentrated sulfuric acid to prepare a novel kind of adsorption gel for gold. The adsorption behaviors of the gel were investigated for various metals from acidic chloride media. The gel was found to be highly selective for Au(III) over other precious and base metals tested over the whole concentration range of hydrochloric acid. The maximum adsorption capacity for Au(III) was evaluated as 6.21 mmol/g at 303 K. The amount of adsorbed Au(III) was increased with increasing temperature. A kinetic study for the adsorption of Au(III) at various temperatures confirmed the endothermic adsorption process following pseudo-first order kinetics. The activation energy was evaluated as 78.8 kJ/mol. Interestingly, it was found that the adsorbed Au(III) was reduced to elemental form which was evidenced by the clearly visible elemental gold particles which was further confirmed by means of the X-ray diffraction spectrum and optical microscope image of the gel after the adsorption of Au(III). The mechanism of Au(III) adsorption on the cotton gel and its reduction to elemental gold was proved from the results of IR-spectra. The main mechanism could be explained in terms of the coordination of Au(III) to oxygen atom of C–O–C linkage of cross linked cotton gel and to the oxygen atoms of the hydroxyl groups at C_2 and C_3 atoms of pyranose ring of cotton cellulose followed by the reduction to metallic gold. The adsorbed gold in the cotton gel can easily be recovered by incineration.

Keywords Cotton · Cellulose · Adsorption · Gold(III) · Kinetics · Thermodynamic parameters

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Introduction

Gold has emerged as one of the most expensive metals reaching a high price in the international market Dephanche and Macaskie (2008). This increasing price of gold with its ever increasing demand is not only due to the jewelry values but also due to the vast application of gold in various high-tech industries (Aworn et al. 2005; Xiong et al. 2009; Adhikari et al. 2007; Yap and Mohamed 2007; Kwak et al. 2010; Ha et al. 2010) for its unique physical and chemical characteristics (Senturk et al. 2007). In recent years, the manufacturing of electronic and electrical devices is a major demand sector for precious metals (Chancerel et al. 2009) like gold. The high pace of technological change

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